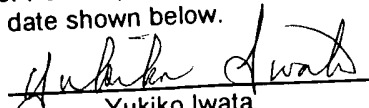


I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to Assistant Commissioner for Patents, Washington, D.C. 20231, on or before the date shown below.

  
Yukiko Iwata  
Date: January 8, 2001



1764 #4  
PATENT  
TS0926 (US)  
YI:EM

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of )

MARIA B. H. VAN CRIJNEN-BEERS, )  
JEAN-PAUL DARNANVILLE, )  
CAROLUS M. A. M. MESTERS, and )  
THOMAS J. REMANS )

Serial No. 09/664,293 )

Filed September 18, 2000 )

METHOD FOR PREPARING A CATALYST )

Group Art Unit: 1764

January 8, 2001

ASSISTANT COMMISSIONER FOR PATENTS  
Washington, DC 20231

Sir:

CLAIM TO PRIORITY

Applicants reaffirm the claim for the benefit of filing date of the following foreign patent application referred to in Applicant's Declaration:

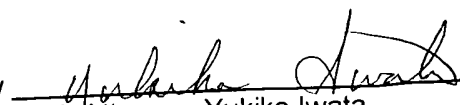
European application Serial No. 99402401.6 filed September 27, 1999

A copy of the application certified by the European Patent Office is enclosed.

Respectfully submitted,

MARIA B. H. VAN CRIJNEN-BEERS,  
JEAN-PAUL DARNANVILLE,  
CAROLUS M. A. M. MESTERS, and  
THOMAS J. REMANS

By

  
Their Attorney, Yukiko Iwata  
Registration No. 35,748  
(713) 241-5593

P.O. Box 2463  
Houston, Texas 77252-2463





Europäisches  
Patentamt

Eur pean  
Patent Office

Office eur péen  
des brevets



Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-  
gen stimmen mit der  
ursprünglich eingereichten  
Fassung der auf dem näch-  
sten Blatt bezeichneten  
europäischen Patentanmel-  
dung überein.

The attached documents  
are exact copies of the  
European patent application  
described on the following  
page, as originally filed.

Les documents fixés à  
cette attestation sont  
conformes à la version  
initialement déposée de  
la demande de brevet  
européen spécifiée à la  
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99402401.6

RECEIVED  
17 JAN 2001  
COMMUNICATIONS CENTER 1100

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN  
THE HAGUE, 20/12/00  
LA HAYE, LE





**Eur päisches  
Patentamt**

**Eur pean  
Patent Office**

**Office européen  
des brevets**

**Blatt 2 der Bescheinigung  
Sheet 2 of the certificate  
Page 2 de l'attestation**

Anmeldung Nr.:  
Application no.: 99402401.6  
Demande n°:

Anmeldetag:  
Date of filing: 27/09/99  
Date de dépôt:

Anmelder:  
Applicant(s):  
Demandeur(s):  
**SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.**  
**2596 HR Den Haag**  
**NETHERLANDS**

Bezeichnung der Erfindung:  
Title of the invention:  
Titre de l'invention:

**Method for preparing a low acidity refractory oxide-bound zeolite catalyst**

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:  
State:  
Pays:

Tag:  
Date:  
Date:

Aktenzeichen:  
File no.  
Numéro de dépôt:

Internationale Patentklassifikation:  
International Patent classification:  
Classification internationale des brevets:

**B01J37/00, B01J29/06, C07C5/27, C10G45/64**

Am Anmeldetag benannte Vertragsstaaten:  
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/~~ES~~  
Etats contractants désignés lors du dépôt:

Bemerkungen:  
Remarks:  
Remarques:

**See for original title page 1 of the description.**



TS 0926 EPC

Crw

## METHOD FOR PREPARING A CATALYST

The invention relates to a method for preparing a catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina.

5        Such a method is described in patent publication  
US-A-5053374 which illustrates the preparation of a  
silica-bound USY catalyst. 65 wt. parts of the zeolite in  
the form of a powder was mixed with 35 weight parts of  
silica consisting of various ratios of an amorphous  
10       precipitated silica (PPG Industries HiSil 233 EP) and a  
basic colloidal silica of the type Ludox HS-30. A  
homogenous mix was obtained by mulling. The moisture  
content of the mix was adjusted to 42-47 weight percent  
with deionized water. The mix was extruded to yield  
15       extrudate. The extrudates were subsequently dried and  
ammonium exchanged to remove sodium and subsequently  
calcined.

When contents of binder and or zeolite are used in  
the context of the present invention the content on a dry  
20       basis is meant. When a pH value is mentioned the pH as  
measured in water of 18 °C is meant.

There remains room to improve the strength of the  
catalyst extrudates as obtained by the process as  
described in US-A-5053374. This is especially true when  
25       catalyst extrudates are made having a zeolite content of  
below 50 wt%. It appears that the strength of the  
catalyst is negatively influenced when the zeolite  
content is reduced. For some applications however a  
zeolite content of well below 50 wt% is advantageous in  
30       terms of improved selectivity and activity of the

catalysed reaction. An example of such an application is the catalytic dewaxing process as described in US-A-5804058. For commercial application it is therefore desirable to be able to prepare such catalysts having a good strength.

The object of the present invention is a process to prepare a low acidity refractory oxide bound zeolite catalyst having a high crushing strength. A further object is to provide a process which enables one to prepare silica bound catalysts of sufficient strength having a zeolite content of below 50 wt%.

The object of the invention is achieved by the following process. A method for preparing a catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina which comprises:

- (a) preparing an extrudable mass comprising a substantially homogenous mixture of zeolite, water, a source of the low acidity refractory oxide binder present as an acid sol and an amine compound,
- (b) extruding the extrudable mass resulting from step (a),
- (c) drying the extrudate resulting from step (b); and,
- (d) calcining the dried extrudate resulting from step (c).

Catalyst particles obtained by the above process have an increased crushing strength. This is advantageous because such catalysts are typically applied in a packed bed reactor. Due to the normally high operating pressure and mass flows in the reactor strong catalyst particles are needed.

Examples of the low acidity refractory oxide binder material which is essentially free of alumina are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these like for example silica-



zirconia and silica-titania. A preferred binder is silica. The description of the invention will further refer to a silica binder only. It will be understood that the below preferred conditions will, when applicable, also apply to other possible binders as here described.

The acid silica sol may be any colloidal silica having a pH lower than 7. An example of a suitable acid silica sol is Nyacol 2034DI which can be obtained from PQ Corp, Valley Forge, Pennsylvania or Ultra-Sol 7H from RESI Inc, Newark. The surface of the acid silica sol particle comprises -OH groups. It is believed that for obtaining a catalyst particle having a sufficient strength it is essential that during the mixing of the components in step (a) some or all of these groups are converted to  $-O^-$  groups. This is achieved by adding the amine compound in step (a). It has further been found that when adding the amine compound just before performing step (b) an even more stronger catalyst particle is obtained. It is believed, although we do not wish to be bound to this theory, that the stronger catalyst is obtained because not all of the -OH groups on the sol particle surface are converted into  $-O^-$  groups. Thus step (a) is preferably performed by first mixing the zeolite and the acid silica sol into a first homogeneous mixture and subsequently adding the amine compound to the first homogeneous mixture such that the pH of the resulting second mixture is raised from below 7 to a value of above 8. It can be easily determined by one skilled in the art, by straightforward experimentation, what the optimal moment in step (a) is for adding the amine compound. As a guideline it is preferred to add the amine compound during the second half of the time and more preferably in the last quarter of the time required to mix the components in step (a). Most preferably the

amine compound is added within 20 minutes before performing step (b).

The extrudable mass in step (a) should have a sufficient viscosity in order to be extruded into shapes.

5 One skilled in the art will know how to achieve such a paste like mixture. For example by adding water in step (a) the viscosity can be lowered. The water content of the sol may be between 60 and 80 wt%. Preferably the water content of the extrudable mass as obtained in  
10 step (a) does not exceed 60%, and preferably is at least 35% by weight.

When preparing catalysts having a lower zeolite content, especially lower than 50 wt%, it becomes more difficult to achieve a sufficient high viscosity and  
15 preferably some of the acid silica sol is replaced by silica powder as the silica source. To obtain the strongest catalysts it is preferred to maximise the amount of acid silica sol used relative the amount of silica powder used, while still achieving a sufficient  
20 viscosity of the extrudable mass. The optimal amount of silica powder to be used will depend on the zeolite content, wherein at a low zeolite content of the catalyst, more silica powder will have to be used. One skilled in the art can easily determine the optimal  
25 composition in view of the above teaching. The silica powder may be commercially obtained silica powder, for example Sipernat 22 or 50 (as obtained from Degussa AG), Nasilco Ultrasil VN3SP or HiSil 233 EP from PPG Industries. The solid silica powder particles preferably  
30 have a mean diameter of between 10  $\mu\text{m}$  and 200  $\mu\text{m}$ .

The amine compound is preferably a compound according to the general formula  $R_1R_2R_3N$  in which  $R_1$ - $R_3$  may be hydrogen and/or an alkyl group having 1-6 carbon atoms. Examples are ammonia, methyl ethyl amine, triethyl amine,

of which ammonia, is the most preferred. The amine compound should preferably be added in such an amount in order to raise the pH of the mass to alkaline conditions. Preferred conditions are a pH of the mixture obtained in step (a) of above 8. The pH will be lower than 14.

Step (a) may for example be performed at ambient conditions by first mixing the zeolite, optionally the silica powder and acid silica sol, subsequently adding an amine compound and optionally at the end of step (a) a plasticising agent. The plasticiser agent is used to increase the viscosity of the mixture in order to obtain an extrudable mass. Suitable plasticising agents are for example dextrose, gelatine, glucose, glues, gums, salts, waxes, starch and cellulose ethers. Some typical cellulose ether binders are methylcellulose, ethylhydroxyethylcellulose, hydroxybutyl methylcellulose, hydroxymethylcellulose, hydroxypropyl methylcellulose, hydroxyethyl methylcellulose, hydroxybutylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, sodium carboxymethylcellulose, and mixtures thereof. Methylcellulose and/or methylcellulose derivatives are especially suited as organic binders in the practice of the present invention with methylcellulose, hydroxypropyl methylcellulose, or combinations of these being preferred. Preferred sources of cellulose ethers are Methocel A4M, F4M, F240, and K75M from Dow Chemical Co.

The extrusion in step (b) may be performed by well known processes as for example illustrated in Perry's Chemical Engineers' Handbook, McGRAW-HILL International Editions, sixth edition, 1984, p 8-60 to 8-66 and in Particle Size Enlargement, Handbook of powder Technology Vol. 1, Elsevier, 1980, p 112-121. Examples of such methods are extrusion performed by a screw extruder, a plate or ram extruder. The extrudates can have a wide variety of forms and sizes.

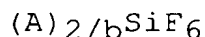
Drying step (c) and calcining step (d) may be performed under conditions well known to one skilled in the art. Step (c), for example, may take place at a temperature of at least 60 °C to about 250 °C, for a time  
5 sufficient to dry the extrudate, for example, for at least 1 hour. Calcining step (d), for example, may take place in air, or other inert gas, at temperatures ranging from 250 °C to 850 °C for periods of time ranging, for example, from about 1 to about 48 hours or more.

10 The method of preparing a low acidity refractory oxide-bound zeolite of this invention is not limited to any particular zeolite and in general includes all metasilicates, particularly the aluminosilicates whether or not previously dealuminized to increase the  
15 framework silica:alumina ratio. Typical zeolites include ZSM-4 (Omega), ZSM-5, ZSM-11, ZSM-12, ZSM-20, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, Beta, X, Y and L as well as ferrierite and mordenite.

Catalysts of improved selectivity and other  
20 beneficial properties can be obtained by subjecting the catalyst extrudates to a dealumination treatment. Dealumination can be attained by methods known in the art, such as for example acid leaching or by a steam treatment. Steam treatment is effected by contacting the  
25 catalyst extrudates with steam at elevated temperatures ranging from about 250 °C to 650 °C and preferably from about 400 °C to 550 °C. The treatment can be accomplished in an atmosphere of 100% steam or in an atmosphere consisting of steam or ammonia and some other gas which  
30 is essentially inert to the zeolites. A similar treatment can be accomplished at lower temperatures and elevated pressure, e.g., from about 180 °C to 370 °C at from about 10 to about 200 atmospheres.

35 Particularly useful dealumination methods are those, wherein the dealumination selectively occurs, or anyhow

is claimed to occur selectively, at the surface of the crystallites of the molecular sieve. Preferably dealumination is performed by a process in which the zeolite is contacted with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:



wherein 'A' is a metallic or non-metallic cation other than H<sup>+</sup> having the valence 'b'. Examples of cations 'b' are alkylammonium, NH<sub>4</sub><sup>+</sup>, Mg<sup>++</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ba<sup>++</sup>, Cd<sup>++</sup>, Cu<sup>+</sup>, Ca<sup>++</sup>, Cs<sup>+</sup>, Fe<sup>++</sup>, Co<sup>++</sup>, Pb<sup>++</sup>, Mn<sup>++</sup>, Rb<sup>+</sup>, Ag<sup>+</sup>, Sr<sup>++</sup>, Tl<sup>+</sup>, and Zn<sup>++</sup>. Preferably 'A' is the ammonium cation. The zeolite material may be contacted with the fluorosilicate salt in an amount of at least 0.0075 moles per 100 grams of the zeolite material. The pH is suitably between 3 and 7. An example of the above described dealumination process is described in US-A-5157191.

The original cations associated with each of the zeolites utilized herein can be replaced by a wide variety of other cations employing techniques well known in the art. Such a replacement of cations is suitably performed after the above described optional dealumination step. Typical replacing cations including hydronium, ammonium, alkyl ammonium and metal cations. Suitable metal cations include metals such as rare earth metals, as well as metals of Groups IIA and B of the Periodic Table, e.g., zinc, and Group VIII of the Periodic Table, e.g., platinum, palladium and nickel.

Typical ion-exchange techniques call for contacting the selected zeolite with a salt of the desired replacing cation. Although a wide variety of salts can be employed, particular preference is given to chloride, nitrates and sulfates. Representative ion-exchange techniques are

disclosed in a wide variety of patents including  
US-A-3140249, US-A-3140251 and US-A-3140253.

Following contact with a solution of the desired  
replacing cation, the catalyst is then preferably washed  
5 with water and dried and/or calcined as for example  
described above for step (c) and step (d).

The catalyst prepared by the method of this invention  
can find utility in a wide variety of processes which are  
both catalytic and non-catalytic. Quite obviously, the  
10 materials can be used as absorbents. Additionally, the  
materials can be used as catalysts for a wide variety of  
hydrocarbon conversions. As is known in the art, a low  
acidity refractory oxide such as silica has low catalytic  
activity such that incorporation of a zeolite in the  
15 silica leads to some unusual effects. The low acidity  
refractory oxide can be used as a support for a catalytic  
material, e.g., a hydrogenation component such as  
platinum, palladium, cobalt, molybdenum, iron, tungsten,  
nickel or mixtures of the same. In addition, the low  
20 acidity refractory oxide-bound zeolite extrudates find  
utility in hydrocracking, isomerization, hydrogenation,  
dehydrogenation, polymerization, reforming, catalytic  
cracking, catalytic hydrocracking, toluene  
disproportionation, and the like. Thus, the extrudates of  
25 this invention can be used with or without added active  
metal components for catalytic cracking, isomerization,  
alkylation, reforming and hydrogenative conversions such  
as hydrocracking, hydrogenation and hydrofining, e.g.,  
desulfurization and denitrogenation. In some types of  
30 hydrocarbon conversions, e.g., hydroprocessing,  
reforming, catalytic cracking and catalytic hydrocracking  
the use of a low-acidity refractory oxide-bound zeolites  
having lower levels of inherent activity than their  
alumina-bound counterparts can result in lower coke  
35 production and significant increases in cycle length.

Catalysts prepared by the process according the invention can be advantageously used as dewaxing catalyst under well known catalytic dewaxing conditions as for example described in above mentioned US-A-5804058.

5 Especially suitable are catalysts wherein the zeolite is ZSM-5, ZSM-12, ZSM-22, ZSM-23 or SZZ-32. More preferably the catalyst extrudate is subjected to a dealumination treatment as described above and even more preferably the zeolite is ion exchanged to incorporate a platinum,  
10 palladium or nickel metal. A preferred catalyst has a zeolite content of below 50 wt%. The lower zeolite level is 10 wt%. Below this level the activity becomes too low for practical application of the catalyst.

The catalyst prepared by according to this invention  
15 may also be suitably be used in a xylene isomerisation process as for example described in US-A-5554274, US-A-4899011, US-A-5689027, US-A-5516956 and WO-A-9616005.

The invention shall be illustrated by the following  
20 non-limiting examples.

#### Comparative Experiment A

On a dry basis, 60 weight parts of ZSM-5 (CBV8014 as obtained from Zeolyst International) were intimately admixed with 15 weight parts of amorphous precipitated  
25 silica powder (Sipernat-50 as obtained from Degussa) and with 25 weight parts of acid colloidal silica (Nyacol 2034DI as obtained from PQ Corporation); a homogenous mix was obtained by mulling. The total moisture content of the mix was adjusted to 55 weight  
30 percent with deionized water.

5 minutes before extruding the mixture a plasticiser agent, Methocel source (containing 2.1 wt% methocel), was added to the extrudable mass in a ratio of 7/100 of Methocel source relative to the zeolite dry mass. The  
35 mixture was extruded to yield cylinder extrudates with a

diameter of 1.6 mm. The extrudates were subsequently dried at 120 °C for typically 2 hours in air and then calcined at 800 °C for 5 hours.

The Flat Plate Crushing Strength was measured by determining the force in N/cm at which the cylinder extrudate was crushed between two parallel flat plates. The cylinder extrudate was positioned between the plates in such that the cylindrical axis was parallel with the plates. This procedure was repeated 40 times and the average force at which crushing was observed was the resulting Flat Plate Crushing Strength (FPCS). In this example a FPCS of 60 N/cm was measured. See also Table 1.

Comparative Experiment B

Comparative Experiment A was repeated except that the ZSM-5 content was 30 wt%, the silica powder content was 35 wt% and the acid silica sol content was 35 wt%. A FPCS of 86 N/cm was measured. As a result of the lower ZSM-5 content as compared to Comparative Experiment A one would expect a lower FPCS. The resulting higher FPCS is a result of the higher content of acid silica sol as compared to Comparative Experiment A. The FPCS is however not high enough for commercial application. A value of higher than 100 N/cm is desirable. See also Table 1.

Comparative Experiment C

Comparative Experiment B was repeated except instead of acid silica sol the same amount of basic colloidal silica of the type Ludox HS-30 was used. The Flat Plate Crushing Strength was 80 N/cm.

EXAMPLE 1

Comparative Experiment B was repeated except that, after mixing the ZSM-5, silica powder and acid colloidal silica, ammonia was added. Ammonia as a 2.5 wt% aqueous solution was added in a ratio of 1/12 ammonia solution relative to the zeolite dry mass. The resulting pH was 8.8. After adding the ammonia the mixing was continued



for 35 minutes before extruding. The Flat Plate Crushing Strength was 122 N/cm. See also Table 1.

#### EXAMPLE 2

5 Example 1 was repeated except that ammonia was added after 35 minutes after mixing the ZSM-5, silica powder and acid colloidal silica. After adding the ammonia the mixing was continued for 10 minutes before extruding. The Flat Plate Crushing Strength was 178 N/cm.

Table 1

Experi- ment	ZSM-5 con- tent (wt%)	Silica powder (wt%)	Silica sol (wt%)	acidity of used silica sol	ammonia added	FPCS (N/cm)
Comp. A	60	15	25	acid	no	60
Comp. B	30	35	35	acid	no	86
Comp. C	30	35	35	basic	no	80
Example 1	30	35	35	acid	35 minutes before extrusion	122
Example 2	30	35	35	acid	10 minutes before extrusion	178



TS 0926 EPC

C L A I M S

1. A method for preparing a catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina which comprises:

- 5 (a) preparing an extrudable mass comprising a substantially homogenous mixture of zeolite, water, a source of the low acidity refractory oxide binder present as an acid sol and an amine compound,
- (b) extruding the extrudable mass resulting from step (a),
- 10 (c) drying the extrudate resulting from step (b); and,
- (d) calcining the dried extrudate resulting from step (c).

2. Method according to claim 1, wherein step (a) is performed by first mixing the zeolite and the acid sol of  
15 the low acidity refractory oxide into a first homogeneous mixture and subsequently adding the amine compound to the first homogeneous mixture such that the pH of the resulting second mixture is raised from below 7 to a value of above 8.

20 3. Method according to claim 2, wherein the amine compound is added in step (a) within 20 minutes of performing step (b).

4. Method according to any one of claims 1-3, wherein the zeolite content, on a dry basis, is below 50 wt% as  
25 calculated on the finished catalyst and wherein the low acidity refractory oxide source used to prepare the extrudable mass in step (a) also comprises a powder of the low oxide refractory source.

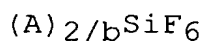
5. Method according to any one of claims 1-4, wherein  
30 the amine compound is ammonia.

6. Method according to any one of claims 1-5, wherein the low acidity refractory oxide binder is silica.

7. Method according to any one of claims 1-6, wherein the zeolite is ZSM-5, ZSM-12, ZSM-22, ZSM-23 or SZZ-32.

5 8. Method wherein the catalyst obtained by the method according to any one of claims 1-6 is subjected to a dealumination treatment.

9. Method according to claim 8, wherein the dealumination treatment is performed by a process in  
10 which the zeolite is contacted with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:



15 wherein 'A' is a metallic or non-metallic cation other than H<sup>+</sup> having the valence 'b'.

10. Method wherein a catalyst obtained by the method according to any one of claims 1-9 is subjected to a cation exchange treatment wherein a palladium, platinum or nickel metal is loaded on the catalyst.

20 11. Use of a catalyst obtained by the method described in any one of claims 1-10 in a hydrocarbon conversion process.

12. Use according to claim 11, wherein the hydrocarbon conversion process is a catalytic dewaxing process or a  
25 xylene isomerization process.

C45/TS0926PD

A B S T R A C T

## METHOD FOR PREPARING A CATALYST

A method for preparing a catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina which comprises:

- (a) preparing an extrudable mass comprising a substantially homogenous mixture of zeolite, water, a source of the low acidity refractory oxide binder present as an acid sol and an amine compound,
- (b) extruding the extrudable mass resulting from step (a),
- (c) drying the extrudate resulting from step (b); and,
- (d) calcining the dried extrudate resulting from step (c).

C45/TS0926PD

